

0SP-11863

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

1026



(43) International Publication Date
7 December 2000 (07.12.2000)

PCT

(10) International Publication Number
WO 00/73227 A1

(51) International Patent Classification⁷:

C03C 8/16

(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(21) International Application Number: PCT/US00/14920

(22) International Filing Date: 31 May 2000 (31.05.2000)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/323,459 1 June 1999 (01.06.1999) US

(71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US).

(72) Inventors: XUE, Liang, A.; 9 Blanchard Ct., Randolph, NJ 07869 (US). JAMES, Piascik; 10 Sandra Lane, Randolph, NJ 07869 (US).

(74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc., 101 Columbia Avenue, P.O. Box 2245, Morristown, NJ 07960 (US).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 00/73227 A1

(54) Title: LOW TEMPERATURE BURNOUT SCREEN PRINTING FRIT VEHICULES AND PASTES

(57) Abstract: A method for making a glass frit paste is provided. First, nitrocellulose is dissolved in a high vapor pressure solvent of the nitrocellulose to make a solution. A portion of the solution is then mixed with alpha-terpineol to form a vehicle. Glass frit is mixed with the vehicle and then ground to form the paste. During the grinding step most of the high vapor pressure solvent evaporates. The resulting paste has a composition comprising about 0.3-12.0 wt. % nitrocellulose, about 0.5-2.0 wt. % of a high vapor pressure solvent of said nitrocellulose, about 14.0-25.0 wt. % alpha-terpineol, and the remainder glass frit.

LOW TEMPERATURE BURNOUT SCREEN PRINTING FRIT VEHICLES AND PASTES

TECHNICAL FIELD

5

This invention relates generally to sealing compositions and in particular to vehicles and pastes for use in the screen printing of glass frit.

10

BACKGROUND OF THE INVENTION

15

Bernot et al, U.S. Patent Application Serial Number 08/986,253, filed December 5, 1997, entitled, (as amended), "Capacitive Pressure Sensor Housing Having a Ceramic Base" which is assigned to the assignee of this application, discloses a glass ceramic capsule comprised of a cover and a header also referred to as a base that together define an interior chamber. A capacitive pressure sensor is mounted within the chamber. The header is ceramic while the cover is either ceramic or metallic. The cover and header are sealed together with glass frit.

20

Typically, the glass frit is made into a paste using a vehicle which is a combination of a solvent and a binder. The paste is then applied onto the surfaces to be bonded by either brushing or ink-jetting. A critical requirement for the vehicle is that it have a low temperature burnout capability. It needs to completely burn out before the glass frit softens (i.e. melts) which occurs at about 350°C (662°F). One vehicle currently used is amyl-acetate (a solvent) containing a small amount of nitrocellulose (a binder). This vehicle meets the temperature requirement because the nitrocellulose burns out well below 350°C (662°F).

25

A disadvantage to the brushing or ink-jetting methods is that with these methods it is difficult to control the thickness and uniformity of the glass frit as

30

WO 00/73227

it is applied. Using a screen-printing method to apply the glass frit paste would provide both performance and cost advantage over these other methods because the screen printing method produces a more uniform frit coating layer with easily controlled thickness and can be economically applied in large scale batch production. However, the current vehicle of amyl-acetate and nitrocellulose is not suitable for a screen-printing method because the evaporation rate of amyl-acetate is too fast creating an unstable paste whose thickness is difficult to control. Further, other commercially available screen-printing vehicles do not burn out completely at temperatures below 350°C (662°F).

Accordingly, there is a need for a low-evaporation rate, low temperature burnout vehicle that can be used in the formation of a glass frit paste that can be used in a screen printing process.

15

SUMMARY OF THE INVENTION

An object of the present invention is to provide a glass frit paste that can be used in a screen printing process and a method for making the paste.

20

Another object of the present invention is to provide a vehicle that can be used in the formation of the glass frit paste and a method for making such a vehicle.

25

To make the glass frit paste nitrocellulose is dissolved in a high vapor pressure solvent of the nitrocellulose to make a solution. A portion of the solution is then mixed with alpha-terpineol to form a vehicle. Glass frit is mixed with the vehicle and then ground to form the paste. During the grinding step most of the high vapor pressure solvent evaporates. The resulting paste has a composition comprising about 0.3-12.0 wt. % nitrocellulose, about 0.5-

2.0 wt. % of a high vapor pressure solvent of said nitrocellulose, about 14.0-25.0 wt. % alpha-terpineol, and the remainder glass frit.

These and other objects, features and advantages of the present invention are specifically set forth in or will become apparent from the following detailed description of a preferred embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A vehicle for use in a screen printing method in applying a glass frit paste comprises alpha-terpineol, nitrocellulose and a solvent of nitrocellulose, such as amyl-acetate or ethylene glycol monoethyl ether. The solvent is transitional in that it mostly evaporates during the paste making process where the vehicle is mixed with glass frit. The use of the solvent is nonetheless essential because the binder, nitrocellulose, does not dissolve in alpha-terpineol. Due to its low-evaporation rate, the resulting paste is stable in open air and suitable for screen-printing. The vehicle burns out at temperatures below 300°C (572°F).

The process to make the vehicle and paste consists of the following steps which preferably occur at room temperature and pressure. First nitrocellulose is dissolved in a high vapor pressure solvent such as amyl-acetate or ethylene glycol monoethyl ether to make a solution. The nitrocellulose preferably constitutes 1 to 15 wt. % of the solution. Next, the solution is mixed with alpha-terpineol. The ratio of solution to alpha-terpineol can range from 1 part solution to five parts alpha-terpineol to 6 parts solution to 1 part alpha-terpineol. The mixing of solution and alpha-terpineol forms the vehicle. The vehicle is then mixed and ground with a glass frit at a ratio that ranges from 2 parts vehicle to 1 part frit to 1 part vehicle to 8 parts frit. A dispersing agent may also be added at this point in the process. The result is

WO 00/73227

the paste. In the preferred embodiment the paste is comprised of about 0.1-18.0 wt. % nitrocellulose; about 0.0-3.0 wt. % of a high vapor pressure solvent; about 8.0-40.0 wt. % ^{21.9C}alpha-terpineol; and the remainder glass frit. In a more preferred embodiment the paste is comprised of about 0.3-12.0 wt. % nitrocellulose; about 0.5-1.9 wt. % of a high vapor pressure solvent; about 14.0-25.0 wt. % alpha-terpineol; and the remainder glass frit. The particular glass frit used is selected to match the expansion properties of the components that are to be sealed together. Examples of such frits are lead borosilicate, copper aluminoborate, lead aluminosilicate, lead zinc borate, zinc borosilicate, zinc bismuthsilicate, alkali zinccsilicate, alkali titaniumsilicate and the like. During the mixing and grinding process, the high vapor pressure solvent, (amyl-acetate or ethylene glycol monoethyl ether), mostly evaporates, that is less than 3 wt. % of the solvent is left in the paste after the process is complete.

15

Examples of the vehicle and paste are set forth below.

EXAMPLE 1

1.90 grams nitrocellulose was dissolved in 51.23 grams amyl acetate to make an amyl acetate solution containing about 3.7 wt. % nitrocellulose. The solution was then mixed with 130.45 grams alpha-terpineol which is a ratio of about 1:2.5 to make the vehicle. 21.8 grams of this vehicle was mixed with 65.0 grams of Corning #2366 glass frit which is a ratio of about 1:4 in a mortar grinder to make a paste to be used in a screen printing process. 4 drops of tridecyl acid phosphate was also added as a dispersing agent. During the mixing/grinding process most of the ^{EoR} amyl acetate evaporates. The final paste is composed of about 0.3 wt. % nitrocellulose, 1.2 wt. % amyl acetate, 19.0 wt. % alpha-terpineol, and 79.5 wt. % glass frit.

EXAMPLE 2

9.86 grams nitrocellulose was dissolved in 161.52 grams amyl acetate to make an amyl acetate solution containing about 5.8 wt. % nitrocellulose. A portion (120.40 grams) of the solution was then mixed with 286.27 grams alpha-terpineol which is a ratio of about 1:2.4 to make the vehicle. 65.42 grams of this vehicle together with an additional 8.19 grams alpha-terpineol were mixed with 186.69 grams of SEM-COM B-10023 glass frit in a mortar grinder to make the paste. The ratio of vehicle to frit of about 1:2.5. 3 drops of tridecyl acid phosphate was also added as a dispersing agent. During the mixing/grinding process most of the amyl acetate evaporates. The final paste is composed of about 0.5 wt. % nitrocellulose, 0.8 wt. % amyl acetate, 22.2 wt. % alpha-terpineol, and 76.5 wt. % the glass frit.

EXAMPLE 3

28.8 grams nitrocellulose was dissolved in 410.3 grams amyl acetate to make an amyl acetate solution containing about 7.0 wt. % nitrocellulose. The solution was then mixed with 481.6 grams alpha-terpineol which is at a ratio of about 1:1.1 to make the vehicle. 34.0 grams of this vehicle together with an additional 8.0 grams alpha-terpineol were mixed with 150.0 grams of SEM-COM B-10050 glass frit in a mortar grinder to make the paste. The vehicle to frit ratio of this example being about 1:3.6. 3 drops of tridecyl acid phosphate was also added as a dispersing agent. During the mixing/grinding process most of the amyl acetate evaporates. The final paste is composed of about 0.6 wt. % nitrocellulose, 0.5 wt. % amyl acetate, 14.5 wt. % alpha-terpineol, and 84.4 wt. % the glass frit.

EXAMPLE 4

2.13 grams nitrocellulose was dissolved in 62.36 grams ethylene glycol monoethyl ether to make an ethylene glycol monoethyl ether solution containing about 3.3 wt. % nitrocellulose. A portion (15.87 grams) of the

WO 00/73227

solution was then mixed with 29.94 grams alpha-terpineol which is a ratio of about 1:1.9 to make the vehicle. It was then mixed with 93.0 grams of Coming #2366 glass frit, a ratio of about 1:2, in a mortar grinder to make the paste. During the mixing/grinding process most of the ethylene glycol monoethyl ether evaporates. The final paste is composed of about 0.4 wt. % nitrocellulose, 0.8 wt. % ethylene glycol monoether 24.0 wt. % alpha-terpineol, and 74.8 wt. % the glass frit.

EXAMPLE 5

10 11.5 gram nitrocellulose was dissolved in 98.5 grams amyl acetate to make an amyl acetate solution containing about 10.5 wt. % nitrocellulose. The solution was then mixed with 20.0 grams alpha-terpineol, a ratio of about 5.5:1, to make the vehicle. It was then mixed with 70.0 grams of SEM-COM B-10050 glass frit which is a ratio of about 1.9:1 in a mortar grinder to make the paste. During the mixing/grinding process most of the amyl acetate evaporates. The final paste is composed of about 11.1 wt. % nitrocellulose, 1.9 wt. % amyl acetate, 19.3 wt. % alpha-terpineol, and 67.6 wt. % the glass frit.

20 Thus a glass frit paste is provided that can be used in a screen printing process resulting in a more uniform frit coating layer with easily controlled thickness. A vehicle used in the formation of this paste is also provided. The vehicle having a low temperature burnout capability below the melting temperature of the glass frit.

25 Various modifications and alterations to the above-described preferred embodiment will be apparent to those skilled in the art. Accordingly, these descriptions of the invention should be considered exemplary and not as limiting the scope and spirit of the invention as set forth in the following claims.

What is claimed is:

1. A method for making a glass frit paste comprising the steps of:
 - 5 dissolving nitrocellulose in a high vapor pressure solvent of said nitrocellulose to make a solution;
 - mixing at least a portion of said solution with alpha-terpineol to form a vehicle; and
 - 10 mixing and grinding at least a portion of said vehicle with glass frit to form the paste, whereby by the end of this step of mixing and grinding most of the high vapor pressure solvent evaporates.
2. The method of claim 1 wherein said nitrocellulose is 1 to 15 wt. % of the solution.
 - 15 3. The method of claim 1 wherein said mixing step includes mixing said solution with said alpha-terpineol at a ratio that is between 1 part solution to five parts alpha-terpineol and 6 parts solution to 1 part alpha-terpineol.
 4. The method of claim 1 wherein said solvent is amyl-acetate.
 - 20 5. The method of claim 1 wherein said solvent is ethylene glycol monoethyl ether.
 - 25 6. The method of claim 1 wherein said step of mixing and grinding includes mixing and grinding the glass frit with the vehicle at a ratio that ranges from 2 parts vehicle to 1 part frit to 1 part vehicle to 8 parts frit.
 - 30 7. The method of claim 1 wherein at the end of the mixing and grinding step less than 3 wt. % of the solvent is left in the paste.

WO 00/73227

8. The method of claim 1 wherein said step of mixing and grinding includes the step of adding a dispersing agent.

5 9. The method of claim 8 wherein said dispersing agent is tridecyl acid phosphate.

10 10. A glass frit paste comprising:
about 0.3-12.0 wt. % nitrocellulose;
about 0.5-2.0 wt. % of a high vapor pressure solvent of said
nitrocellulose;
about 14.0-25.0 wt. % alpha-terpineol;
and the remainder glass frit.

15 11. The glass frit paste of claim 10 wherein said solvent is amyl-acetate.

12. The glass frit paste of claim 10 wherein said solvent is ethylene glycol monoethyl ether.

20 13. The glass frit paste of claim 10 wherein said glass frit is lead borosilicate.

14. The glass frit paste of claim 10 wherein said glass frit is copper aluminoborate.

25 15. The glass frit paste of claim 10 wherein said glass frit is lead aluminosilicate.

30 16. The glass frit paste of claim 10 wherein said glass frit is lead zinc borate.

17. The glass frit paste of claim 10 wherein said glass frit is zinc borosilicate.

5 18. The glass frit paste of claim 10 wherein said glass frit is zinc bismuthsilicate.

10 19. The glass frit paste of claim 10 wherein said glass frit is alkali zincsilicate.

15 20. The glass frit paste of claim 10 wherein said glass frit is alkali titaniumsilicate.

21. The glass frit of claim 10 further comprising at least one drop of a dispersing agent.

22. The glass frit of claim 21 wherein said dispersing agent is tridecyl acid phosphate.

20 23. A vehicle for using in making a glass frit paste for use in a screen printing process comprising:

about 0.1-13.0 wt. % nitrocellulose;
about 14.0-85.0 wt. % of a high vapor pressure solvent of said nitrocellulose;

25 and the remainder alpha-terpineol.

24. The vehicle of claim 23 wherein said solvent is amyl-acetate.

25. The vehicle of claim 23 wherein said solvent is ethylene glycol monoethyl ether.

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 00/14920

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C8/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C04B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 801 108 A (HUANG RONG-FONG ET AL) 1 September 1998 (1998-09-01) column 4, line 63 -column 5, line 43; claims	10,13, 21,23
X	US 5 840 107 A (SALIBAY BERNARDO B) 24 November 1998 (1998-11-24) column 2, line 66 - line 63	10, 13-15,23
A	EP 0 092 601 A (OKUNO CHEM IND CO) 2 November 1983 (1983-11-02) page 6, line 23 -page 8, line 11	1-25 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 September 2000

Date of mailing of the international search report

15/09/2000

Name and mailing address of the ISA
European Patent Office, P.O. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 00/14920

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 293 (C-315), 20 November 1985 (1985-11-20) & JP 60 137848 A (HITACHI SEISAKUSHO KK), 22 July 1985 (1985-07-22) abstract _____	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/14920

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
US 5801108	A 01-09-1998	NONE			
US 5840107	A 24-11-1998	NONE			
EP 0092601	A 02-11-1983	JP 1622035 C			09-10-1991
		JP 2047545 B			22-10-1990
		JP 58189365 A			05-11-1983
JP 60137848	A 22-07-1985	NONE			

